

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08F 265/06, C08K 3/22, C08L 31/02</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/13402</b> <b>(43) International Publication Date:</b> 2 April 1998 (02.04.98)
<b>(21) International Application Number:</b> PCT/US97/04344 <b>(22) International Filing Date:</b> 17 March 1997 (17.03.97)  <b>(30) Priority Data:</b> 08/720,164 25 September 1996 (25.09.96) US  <b>(71) Applicant:</b> ARISTECH CHEMICAL CORPORATION [US/US]; 600 Grant Street, Pittsburgh, PA 15219-2704 (US).  <b>(72) Inventors:</b> MINGHETTI, Ettore; 8739 Heritage Drive, Florence, KY 41042 (US). EITEL, John, E.; 11 Sycamore Drive, Florence, KY 41042 (US). WETTER, Carol, A.; 12216 Gaines Way, Richwood, KY 41094 (US).  <b>(74) Agent:</b> GAVLIK, Robert, R.; Aristech Chemical Corporation, Law Dept., 600 Grant Street, Pittsburgh, PA 15219-2704 (US).		<b>(81) Designated States:</b> CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> THERMOFORMABLE ACRYLIC SHEET HAVING UNIFORM DISTRIBUTION OF COLOR AND MINERAL FILLER  <b>(57) Abstract</b>  A composition suitable for making thermoformable sheets and the like. The composition comprises a cross-linked poly (methyl methacrylate) typically having uncross-linked poly (methyl methacrylate) dispersed therein. The composition comprises 0.5 to about 1.0 pph of at least one cross-linking agent x, and up to about 0.58x-0.28 pph of a at least one chain terminator. The composition also comprises about 0.1 to 8 pph poly (methyl methacrylate) compatible plasticizer, and has about 20 to 60 wt.% solid particle dispersed therein.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
HJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

THERMOFORMABLE ACRYLIC SHEET HAVING UNIFORM  
DISTRIBUTION OF COLOR AND MINERAL FILLER

RELATED U.S. APPLICATION DATA

This is a Continuation-in-Part of Ser. No. 392,650, May 28, 1996, Patent No. 5,521,243, which is a Continuation-in-Part of Ser. No. 157,253, Nov. 26, 1993, abandoned.

Technical Field

This invention relates to poly (methyl methacrylate) ("PMMA") containing compositions useful in the manufacture of sheets or slabs, and methods of manufacturing said sheets. These sheets find use in such applications as kitchen countertops. In addition to PMMA, the above compositions comprise at least one crosslinking agent and at least one chain transfer agent. The concentration of said transfer agent is independent on said crosslinking agent. In the present invention, the amount of chain transfer agent is lower than prior art compositions due to the addition of a small amount of plasticizer. The sheets also contain a significant amount of flame retardant minerals such as alumina trihydrate, and typically contain colorants. These colorants are often used for imitation of natural minerals such as onyx, marble, or other solid color or patterned types having no visibly distinguishable particles. The sheets of the present invention can be heat bent, or thermoformed at an angle as sharp as ninety degrees and/or can be vacuum thermoformed into shapes such as sinks and bowls.

shapes such as sinks and bowls.

#### Background of the Invention

Sheets (used herein interchangeably with slabs) of synthetic mineral appearing material are commonly used as kitchen countertops and interior and/or exterior decorative coverings for buildings and the like. Often the design specifications require sheets to be fitted together or otherwise abut another surface at ninety degree angles.

The fabrication process required under these conditions is both time consuming and expensive. Often there are color differences between abutting surfaces, and the point of contact may be esthetically unappealing. The sheets of the present invention can provide a complex finished part by simple thermoforming operations. For example, to form a vanity top having a ninety degree back splash wall and a front end bull nose of 1.0 inch radius. After forming, cooling and trimming, the part can be installed directly without additional fabrication.

U. S. Patent 3,563,939 and Canadian Patent 916,337 disclose the use of alumina trihydrate ("ATH") in poly (methyl methacrylate) ("PMMA") articles. In U. S. Patent 3,847,865 Duggins discloses the construction of synthetic mineral products. Duggins also discloses the use of crosslinking and mold release agents as well as viscosity reducers such as aliphatic acids.

Buser et al, in U. S. Patent Nos. 4,085,246 and 4,159,301, discloses the phenomena of particle settling rates suitable for making synthetic granite having a polymerizable methyl methacrylate ("MMA") matrix and PMMA dissolved

therein. The PMMA is used to adjust the viscosity which in turn controls the settling rates of the larger particles. The patents further disclose the use of chain-transfer agents as accelerators for polymerization (see '301 at col.8, lines 58-68). The drawback to these patents is that the sheets cannot be thermoformed to the same extent as the sheets of the present invention.

In Gavin et al, U. S. Patent 4,413,089; uniformity of color is disclosed as an objective. Iron oxide pigment of ten microns or less is uniformly distributed in a syrup of MMA/PMMA. The syrup is then cured.

More recently, Minghetti et al, in U. S. Patent 5,521,243, disclose a composition for making thermoformable sheets. A reference point one-half inch sheet is disclosed as having a minimum bending radius of less than three inches. However, that composition is limited in that when the amount of crosslinking agent "x" is 0.5 pph or more, the amount of chain terminator is no less than 0.58x-0.28 pph. In contrast, the composition of the present invention is drawn to a thermoformable sheet wherein the composition is such that the amount of chain terminator is less than 0.58x-0.28 pph. The composition, and thus the sheets manufactured therefrom, have the unexpected feature of performing almost identically to the '243 composition, but at ratios of crosslinker to chain terminator not thought possible in the '243 invention. The difference is attributable to the addition of at least one plasticizer to the instant composition.

#### Brief Description of the Drawings

FIG. 1A is a more or less hypothetical illustration of a prior art bending of a one-half inch thick sheet of a contemporary commercial product

"Corian" (by DuPont).

FIG. 1B is a similar illustration of the bending of a one-half inch thick sheet of the present invention.

#### Summary of the Invention

The present invention is drawn to compositions, thermoformable sheets and thermoformed articles made therefrom. As used herein, by MMA and PMMA is meant a mixture comprising mainly methymethacrylate monomer or polymethylmethacrylate polymer respectively. Other co-monomers or copolymers such as butyl acrylate, ethyl acrylate may be present in total amounts up to about twenty percent of the polymerizable portion of the composition. The weight average molecular weight of the PMMA is typically 30,000 to 600,000 and having little or no crosslinked polymer chains to maintain its solubility in MMA. The MMA is typically at least 60 to 80% monomer having about 20 to 40% polymer dissolved therein. However, the monomer content can be in excess of 90%.

The sheets can be heat bent at relatively sharp angles and can be thermoformed into shaped articles without losing the uniform appearance and properties of the top surface. The sheets undergo only minor tolerable color changes across the entire finished part, either less than  $\Delta E = 2.0$  by Cielab, or not easily discernible by the human eye. The thermoforming temperature is low enough to avoid any significant loss of water from the ATH filler during thermoforming, as is often the case with other thermoplastic materials. The sheet will have a Flame Spread Index, by the ASTM E-84 Tunnel Test lower

than 75 and a Smoke Index of 350 or less. The sheet will also have a relatively equal impact resistance, as measured by a falling weight method, as measured from both the top and bottom side.

The present invention provides for the stability of the suspension of alumina trihydrate in a syrup of MMA having PMMA dissolved therein as follows (by weight):

(a) Content of PMMA dissolved in MMA: 0-30 wt%, preferably 10-25wt%;

(b) ATH in the entire composition: 20-60 wt%, preferably 25-40 wt%;

(c) thixotropic agent (preferably fumed silica) in the monomer/syrup fraction: 0.10-3.5 wt%, or as much as necessary to obtain a viscosity of 1,000-10,000 cps (preferably 2,000-5,000 cps) after mixing, as measured by Brookfield Viscometer Model RVTDV-II, Spindle No. 2, 10RPM;

(d) crosslinking agent as wt% of the total monomer content: greater than 0.5 up to about 1.0 wt% for ethylene glycol dimethacrylate, equivalent content for other crosslinking agents, preferably 0.5 to 1.0 wt%;

(e) chain-transfer agent as wt% of total monomer content up to  $0.58x - 0.28$ , where  $x$  is the amount of crosslinking agent in pph of ethylene glycol dimethacrylate equivalents, and wherein the amount is based on n-dodecyl mercaptan (other agents may vary the exact content slightly to give results equivalent to n-dodecyl mercaptan);

(f) about 0.1 to about 8 phr (parts per hundred of resin composition) of at least one plasticizer.

As shown above, the crosslinking and chain-transfer agents'

concentration will vary slightly depending on the exact agents selected. One way to compare the effects of chain transfer agents is to polymerize MMA in the presence of said agents and in the absence of crosslinkers. The MW<sub>w</sub> and MW<sub>n</sub> should be similar to that obtained by n-dodecyl mercaptan. In addition to the above, other ingredients such as dyes, pigments, polymerization initiators may be present. These additional ingredients are well known in the art.

The particulates of the present invention will not be visibly distinguishable in the finished product. Most synthetic granites will contain visibly distinguishable particles of various compositions and colors ranging from 150 to 500 microns. That is, passing through a sieve having openings of 500 microns, but retained on a sieve of openings less than 150 microns. However, larger particles are also used in the art. In the present invention, the use of larger particles can inhibit the even distribution of said particles. In the context of the present invention the majority of particles will be less than about 90 microns, and preferably are mostly less than about 60 microns. The particles' composition is preferably ATH, but may be any composition having similar properties, in particular the flame retardant properties of ATH. , it should comprise 25 to 50 weight percent.

The solid surface material of the present invention will typically have a somewhat glossy appearance attributable to the acrylic surface. The particulates will not be discernable, as with simulated granite surfaces, and the appearance can be described as substantially fine grained.

Any number of crosslinking agents, di-functional or tri-functional , may be used. Examples include, but are not limited to the following: ethylene glycol



dimethacrylate, propylene dimethacrylate, polyethylene-glycol dimethacrylate, divinyl benzene, diallyl phthalate, 1,3-butanediolmethacrylate, 1,4-butane ethylene glycol dimethacrylate, neopentyl glycol dimethacrylate, trimethacrylate, triallyl cyanurate, pentaerythritol tetramethacrylate, allylmethacrylate, hydroxypropylmethacrylate and hydroxyethyl methacrylate. Preferably, ethylene glycol dimethacrylate is used. Preferably, the amount of crosslink will be at least .01% to about 10%.

Chain terminator or chain-transfer agents include, but are not limited to the following: octyl mercaptan, iso-dodecyl mercaptan, thiurams, dithiocarbamates, dipentene dimercaptan, 2-mercapt ethanol, allyl mercapt-acetates, ethylene glycol dimercapt-acetate, trimethylolethane trithioglycolate, and pentaerythritol tetrathioglycolate. In the present invention the chain terminator serves to regulate the length of the polymer chains and thus to obtain a suitable polymer matrix for thermoforming. Preferably the amount of chain transfer agent used will be at least 0.01% n-dodecyl mercaptan.

The present invention is not limited to a particular subclass of plasticizer provided said plasticizer is compatible with an MMA/PMMA syrup. Any compatible plasticizer known in the art is contemplated by the present invention. The plasticizers included in the present invention will have the feature of lowering the Heat Distortion Temperature (ASTM D-648) of the base formulation. The plasticizers selected can be either monomeric or polymeric. Monomeric plasticizers include phthalates, epoxies, adipates, azelates, trimellitates, glutarates, and citrate esters. These plasticizers are commonly used due to their low cost and suitability to typical applications. Polymeric

plasticizers generally consist of polyesters of dibasic fatty acids and polyfunctional alcohols. Extensive lists of MMA/PMMA compatible plasticizers exist in the art. Also, liquid fire retardants containing P, Cl, Br, and the like are understood in the art to plasticize polymeric compositions, and are therefore incorporated in the context of the present invention. At least one plasticizer is added in an amount of about 0.1 to about 8 phr. Preferably, in the amount of about 2 to about 8 phr.

Conventional thickening agents as well as thixotropic agents are particularly suited to the present invention. They are believed to enhance the inertial tendency of a particle to remain stationary in the matrix suspension. Preferably, fumed silica is used. By fumed silica is meant the product formed by the hydrolysis of silicon tetrachloride vapor in a flame of hydrogen and oxygen, to produce solid particles in the range of about seven to 30 millimicrons. Several commercial types of fumed silica are available. The majority of experimentation for the present invention was conducted with CAB-O-Sil M5, which has a surface area of 200 square meters per gram. However, the present invention is not limited to any one particular type.

The surface of fumed silica is hydrophilic due to an abundance of hydroxyl groups. Absorbed moisture in the silica, or in the other components has a gross effect on the final viscosity of the suspension, and normally lowers the viscosity. The same effect can be achieved with other substances which are more or less capable of developing hydrogen bonding.

If the fumed silica and/or ATH are dried to eliminate the absorbed moisture, the final viscosity of the suspension will be higher. However, drying

the ATH above 200° F may hinder its utility as a flame retardant by depleting its water content.

In our preferred compositions, the amount of fumed silica is selected so that the preferred viscosity is obtained, regardless of variations in the other ingredients.

The preferred method of obtaining a desired viscosity is the following:

(A) Mix all the ingredients (MMA, PMMA, ATH, pigments, other additives, catalysts, chain-transfer agent, crosslinking agent, and plasticizer) of the formulation except the fumed silica and measure the viscosity as indicated below. If necessary, adjust the MMA (monomer) content of the syrup to obtain a viscosity of 800 to 1,500 centipoise.

(B) Repeat step A including an amount of fumed silica and measure the viscosity.

(C) Repeat step B to bring the viscosity to a level between 1,000 and 10,000 centipoise, preferably between 2,000 and 5,000 centipoise.

Hellsund's U.S. Patent No. 3,371,383 and Opel's U.S. Patent No. 3,376,371, are incorporated herein by reference in their entireties, as these references represent our preferred procedure for formation of sheet material or a continuous cast operation. While the forming of sheets between two moving continuous steel belts is the preferred procedure, it is important to realize that such machines are necessarily prone to vibration and microadjustments which tend to result in an almost unavoidable jostling of the particulates in the syrup; the concentrations of crosslinker, chain terminator, fumed silica, and PMMA prepolymer factor in stabilizing the ATH and/or other solids contributing to an

evenly distributed fine-grained appearance.

#### Detailed Description of the Invention

Referring now to FIG. 1A, the recommended (DuPont "Corian" Technical Bulletin CTDC-110, October, 1987) minimum bending radius of three inches for a prior art one-half inch thick flat sheet is illustrated as the radius of the bend in the inside curve from vertical extension point A to horizontal extension point B. Applying the simple formula  $C = \pi D$ , the circumference of a hypothetical three-inch circle would be 18.8496 inches, and the quarter circle AB would measure 4.7124 inches. Applying the same formula to the outside curve for a sheet 0.5 inch thick, i.e. using a radius of 3.5, yields a quarter circle of 5.4953, a difference of 16.6% from the inside curvature. Such a distortion will tend to cause a flow of heated ingredients from the compressed inside curve to the expanded outside, and lengthwise toward points A and B from the curved portion. The flow of ingredients has a tendency to distort the visual or decorative pattern; accordingly, the prior art has minimized the disruptions of the material by using a relatively large radius for the curvature, eg. 3 inches.

FIG. 1B illustrates the achievable curvature of a sheet of the present invention, wherein the radius of the curve is one-half inch rather than the three inches of the section of FIG. 1A. In this case, the theoretical circumference of the outside of the curved section CD is 100% greater than that of the inside of the curve. It is readily seen that by enabling such a forming ability, the present invention overcomes a more severe displacement of material in relatively less volume. The relatively more severe displacement of material means a greater

potential for distortion of the esthetic pattern, but we avoid or neutralize such distortion and so achieve a continuity of pattern heretofore not achievable under the stress of thermoforming.

A test has been devised to evaluate thermoformability, which is a primary object of the present invention. The test consists of clamping a flat test specimen  $4 \frac{7}{8}$  square having the desired thickness onto a steel plate in which has been drilled a 3-inch diameter hole; then a polished stainless steel plunger having a one-inch radius is lowered at a rate of five inches per minute regardless of the resistance. The apparatus and sample are heated prior to the test to the desired temperature. As the plunger moves, a load cell generates a signal representing the amount of resistance in pounds, which may be recorded. At the moment the specimen ruptures, the plunger is stopped and the distance it has traveled is measured. Averaging of tests from four specimens of each sample is recommended. This test may be referred to herein as TP-0085.

The invention is illustrated by, but not limited to the following example:

Example 1

Sheet samples of 0.500" thickness were prepared as described in Example 3 of U.S. Patent No. 5,521,243, from a basic formulation consisting of:

---

	% Weight
ATH (Solem OE-431)	40
MMA/PMMA (20%) Syrup	59.75
BYK 1142	.25
n-dodecyl mercaptan	0.119 phr <sup>(*)</sup>
Ethylene glycol dimethacrylate	0.135 phr <sup>(*)</sup>
Catalysts	As needed
pigments	As needed
other additives	As needed

---

<sup>(\*)</sup>These amounts correspond to .249% and .282%, respectively, of the MMA present in the formulation.

The samples were poured between two casting plates made of stainless steel, to produce 12" x 12" sheets of 0.500" thickness after curing. The curing was obtained by dipping the stainless steel plate assembly into a water tank kept at 180°F. For one hour and then into an air circulating oven, kept at 250° F., for one hour. This was done to evaluate laboratory prepared formulations in which variations of the amount of chain transfer (n-dodecyl mercaptan) and crosslinking agents (ethylene glycol dimethacrylate) were made.

Samples 1A, 1B, and 1C were made from the formulation above, with Epoxol 9.5 (epoxidized linseed oil produced by ACS, Inc.) Added as indicated in the table below.

Samples 1G and 1H contained 2 and 4 phr, respectively, of Fyrol RDP, a flame retardant additive containing phosphorus and sold by AKZO. The samples were tested by the thermoforming test method TP-0085, 40 minutes at 340° F. The details of the compositions and the results are listed below:

TP-0085				
Sample ID Thickness	Added phr of	HDT °F(*)	Inches at Break	Lbs. Force at Break
At 320° F./40 min.				
1A/.500"	4.2 of Exoxol 9.5	164.5	13.1	72
1B/.500"	3.0 of Epoxol 9.5	183.9	11.5	99
1C/.500"	1.8 of Epoxol 9.5	192.9	10.7	122
1G/.500"	2 of Fyrol RDP	Not determined	4.4	46
1H/.500"	4 of Fyrol RDP	Not determined	4.6	40

(\*)Heat Distortion Temperature, at 264 psi, per ASTM D-648

Examples 1A, 1B and 1C show a higher degree of stretch of the sheet at a lower force.

In Examples 1G, 1H a commercial flame retardant added to the formulation shows how the termoforming parameters can be modified while adding flame retardant additives which might be categorized as plasticizers.

Epoxol 9.5 is an epoxidized linseed oil, sold by Swift Chemical Company. Fyrol RDP is a bis-phosphate ester, containing 11% of phosphorus and it is sold by AKZO.

#### Example 2

A syrup was made by partial polymerization of MMA to obtain a viscosity of 3 Poise and a PMMA content about of 20% weight. Butyl Acrylate, Cab-O-Sil M5, Aluminum Trihydrate (ATH) we added to the syrup under agitation. Their proportions are indicated below, together with the chemicals necessary to obtain a complete polymerization and a good release from the call casting plates:

	<u>% Weight</u>
I-3 syrup (20% PMMA)	57.20
Butyl Acrylate	2.00
Cab-O-Sil M5	0.53
ATH	39.92
Wetting Agents	0.35
	<u>phr</u>
Pigment Paste	As needed
Release Agents	As needed
Catalysts	As needed
Chain Transfer Agent	See Table A
Crosslinker	See Table A
Plasticizer	See Table A

The mixture of ingredients was handled and polymerized as described in Example 1.

Table A shows the combinations of chain transfer agent, crosslinker and plasticizer used and the test results:

TABLE A

<u>phr on</u> <u>Total Monomers</u>				<u>Heat</u> <u>Dist.</u> <u>Temp.</u> <u>(°F)</u>	<u>TP-0085(*)</u>	
<u>Chain</u> <u>Transfer</u>	<u>Crosslinker</u>	<u>Plasticizer</u>			<u>Inches</u> <u>at</u> <u>Break</u>	<u>Lbs. Force</u> <u>at</u> <u>Break</u>
PL-0	.1	.9	--	200.1	3.3	301
PL-1	.1	.9	4	168.8	3.2	250
PL-2	.1	.7	--	195.2	3.7	258
PL-4	.1	.7	6	155.5	3.8	206

(\*)Tested at 340°F/40 minutes heating time.

The data of Table A shows how a certain amount of plasticizer reduces the force needed for thermoforming, see lbs. force of test PL-1 and PL-4 against PL-0 and PL-2, 250 and 206 lbs. against 301 and 258 lbs. respectively. The PL-0 and PL-2 points are outside the region of compositions claimed in U.S. 5,521,243. If a



plasticizer is added to them, the performance of the sheet changes and it becomes a candidate for thermoforming, since a lower force is necessary to change its shape and obtain acceptable details in the molded sheet.

CLAIMS

## 1. A composition comprising:

(a) a syrup comprising methyl methacrylate and having a polymerizable portion;

(b) 0.5 to about 1.0 parts per hundred, based on the weight of the polymerizable portion, of a crosslinking agent x, said crosslinking agent being dispersed within said syrup;

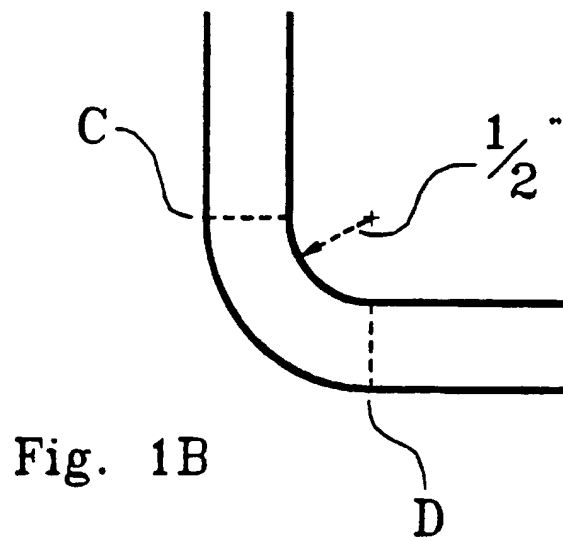
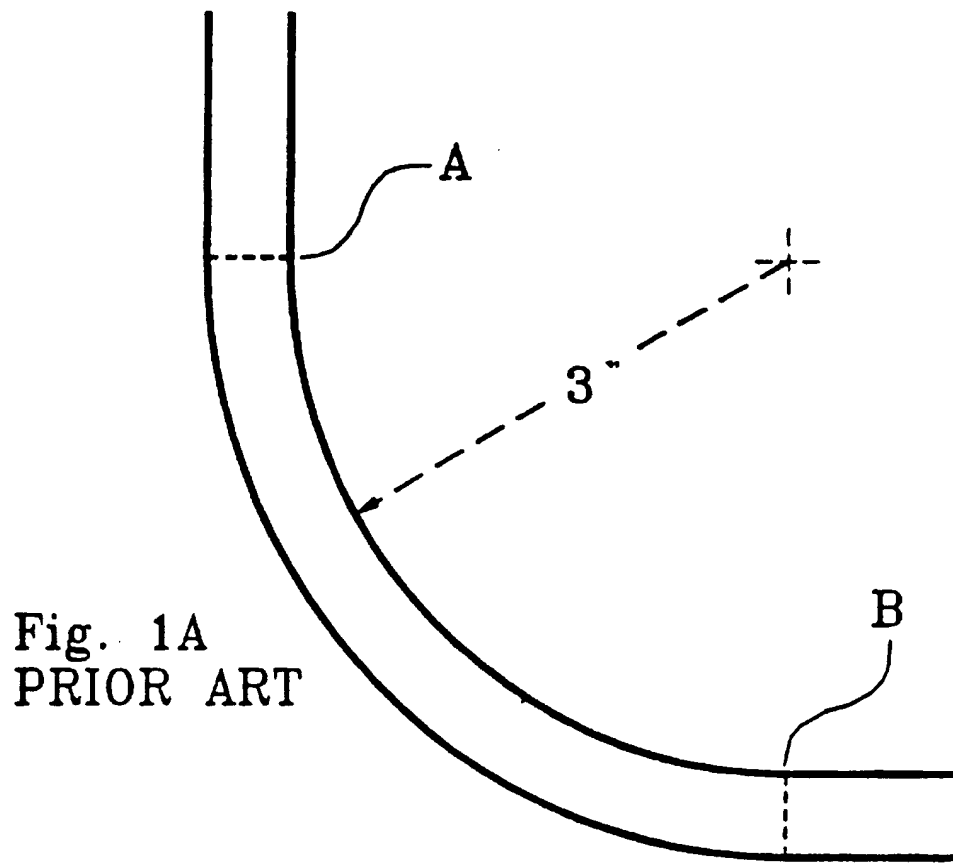
(c) y parts per hundred of a chain terminator, based on the weight the polymerizable portion, said chain terminator being dispersed within said syrup, and wherein y is less than  $0.58x - 0.28$ ;

(d) about 0.1 to 8 parts per hundred, based on the weight of the polymerizable portion, of at least one poly (methyl methacrylate) compatible plasticizer; and

(e) a plurality of solid particles, said particles passing through a sieve having openings of 90 microns, said particles comprising about 20 to 60 wt% of said composition, and wherein a one-half inch thick flat sheet made from said composition will have a minimum bending radius of less than three inches.

## 2. A composition according to claim 1 wherein said solid particles comprise alumina trihydrate.

3. A composition according to claim 1 wherein said chain terminator is n-dodecyl mercaptan.
4. A composition according to claim 1 wherein said crosslinking agent is ethylene glycol dimethacrylate.
5. A composition according to claim 1 wherein said plasticizer is Epoxol 9.5.



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/04344

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C08F 265/06; C08K 3/22; C08L 31/02

US CL : 523/202; 524/437; 525/261, 302, 309

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/202; 524/437; 525/261, 302, 309

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US 5,567,745 A (MINGHETTI et al) 22 October 1996, see entire document.	1-5
A	US 5,521,243 A (MINGHETTI et al) 28 May 1996, see entire document.	1-5

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 30 APRIL 1997	Date of mailing of the international search report 30 MAY 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer MARGARET GLASS
Facsimile No. (703) 305-3230	Telephone No. (703) 308-2351